

# Differences in Naphthalene Soil Concentrations Between Methods 8260 and 8270

INTERNAL DOCUMENT

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## Introduction

The loss of Volatile Organic Compounds (VOCs) during field sampling and laboratory analytical processes is a great concern in the environmental remediation industry because the loss of these compounds leads to low-biased sample results (ILEPA 2020). These low-biased results lead to the potential for false negative determinations of the need for remedies where unacceptably high exposures to contaminants by human and ecological receptors are left in the environment with long-term health consequences.

VOC soil samples are typically taken in the field using EPA Method 5035 to minimize the losses to the atmosphere by collecting the samples as quickly as possible, placing them in air-tight containers with no headspace (e.g., TerraCore® samplers), and adding preservatives, such as methanol and sodium bisulfate, and putting the samples on ice (<https://19january2017snapshot.epa.gov/sites/production/files/2015-12/documents/5035.pdf>) and analyzing them within 14 days. Alternatively, samples can be collected using EnCore® samplers and analyzed within 48 hours, but the VOCs are extracted by methanol or other water-miscible solvents and using methanol preservative in the field is recommended. Conversely, Semi-Volatile Organic Compound (SVOC) soil samples are typically homogenized in the field and placed in a jar with some available headspace and only ice is used as a preservative (EPA 2014). In the lab, the VOC soil samples are analyzed using gas chromatography/mass spectrometry (GC/MS) following EPA Method 8260, whereas SVOC soil samples are analyzed using GC/MS following a version of EPA Method 8270. VOCs will typically be analyzed using 8260C or 8260D, whereas SVOCs are analyzed using Method 8270C, 8270D or 8270E. Generally, Naphthalene would be extracted from the soils in the lab using EPA method 3561 for PAHs before being analyzed using 8270 methods. However, the GC/MS has difficulty achieving low detection limits for Polycyclic Aromatic Hydrocarbons (PAHs), such as Benzo(a)pyrene and Naphthalene, which is usually overcome by using the Selected Ion Mode (SIM) of the GC/MS to increase sensitivity by focusing the analysis on the masses of the PAHs and ignoring the heavier SVOCs (Mills, 2020).

Personnel with the WVDEP Office of Environmental Remediation (OER) have expressed concerns that the process of homogenizing the soils before collecting the SVOC samples may lead to some losses due to volatilization, especially of lower molecular weight compounds like Naphthalene. A literature search has revealed no data or studies that have specifically addressed the potential losses of SVOCs from soils during the homogenization process. Naphthalene is more volatile than other SVOCs and can be analyzed using either the 8260 VOC method or the 8270 SVOC method (Jia and Batterman 2010). Thus, OER decided to compare the concentrations of Naphthalene in soils from sites that presented both the 8260 and 8270 lab method results as a proxy to determine if there might be potential concerns in using either methodology, especially a potential low-bias with method 8270 due to volatilization.

OER personnel looked at the Site Assessment Reports, Risk Assessment Reports or Laboratory Reports for the dozens of the sites in the Voluntary Remediation Program (VRP) and UECA-LUST program to find results for Naphthalene using both the 8260 and 8270 methods from the same sample location. The 8270 method was also separated into SIM and non-SIM results. If the soil homogenization

process routinely causes the volatilization of SVOCs, then the 8270 method concentrations should be significantly lower than the 8260 concentrations, although volatilization may not be the only factor leading to any potential differences.

## Methods

The soil data of 125 VRP and UECA/LUST sites were assessed to determine if they had both 8260 and 8270 lab results for Naphthalene. Of those 125 sites, nine of them had both 8260 and 8270 data; Alker Tire, Brake Supply Co., Elk Terminal, Ohio River Terminals, Supertane, Tri-State Petroleum, Union Carbide Hastings, Jane Lew Halliburton and Elkview Halliburton. Alker Tire and the two Halliburton sites used a non-SIM 8270 method to analyze for Naphthalene, but all other sites used 8270-SIM.

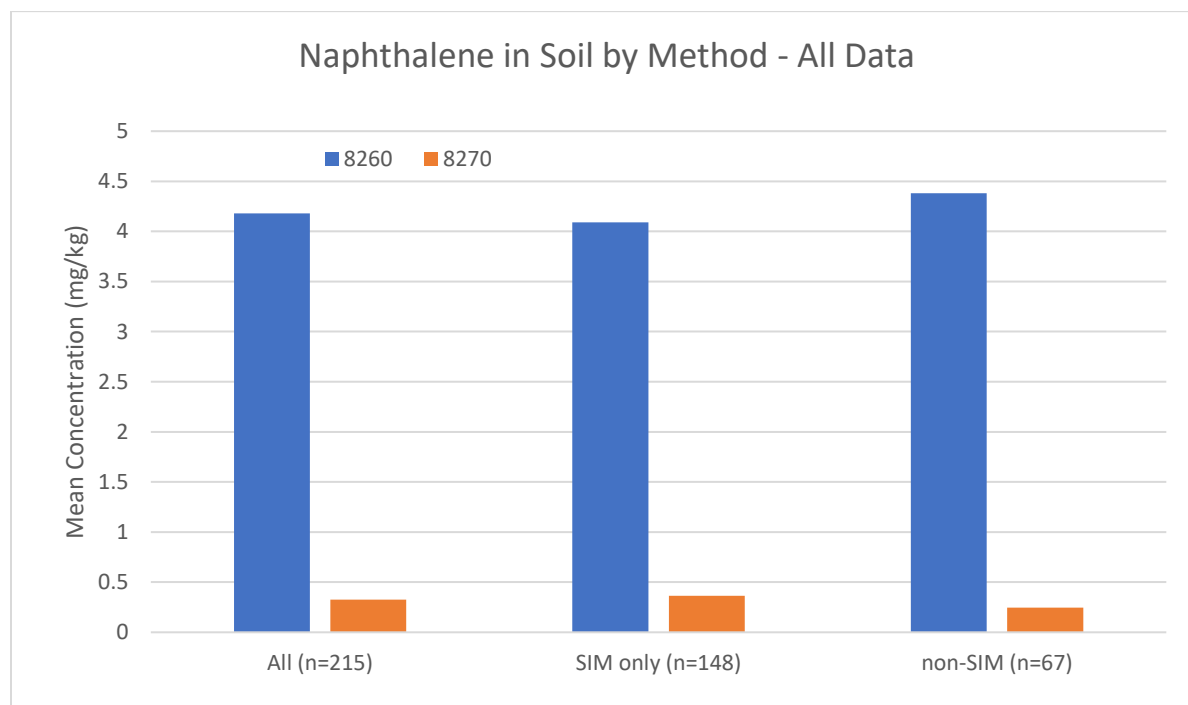
Most of the 8260 and 8270 data pairs had at least one non-detection, which lead to problems with statistical comparisons. Thus, comparisons were done using the Wilcoxon-Mann-Whitney (WMW) test. The dataset was also reduced to just the data pairs that had detections in order to determine impacts on programmatic decisions for the same sample locations. Both the 8260 and 8270 methods and two-tailed WMW tests were used to compare the concentrations of the two methods as well as the concentrations of the 8260 to the 8270-SIM data. WMW was used because both datasets were far from normally distributed and it allowed the non-detect values to all be entered as zero (0) without changing their ranks. Histograms were also used to graphically show the differences between the 8260 and 8270 datasets using the paired data where both methods had detections and also using data where the results were less than 1.0 mg/kg. All statistical analyses were conducted in ProUCL 5.1 with a statistical significance level of  $\alpha = 0.05$ .

## Results

There were 215 samples that had analyses of Naphthalene using both the 8260 and 8270 methods; 22 from Alker Tire, 15 from Brake Supply Co., 18 from Elk Terminal, 26 from Ohio River Terminals, 25 from Supertane, 27 from Tri-State Petroleum, 37 from Union Carbide Hastings, 32 from Jane Lew Halliburton, and 13 from Elkview Halliburton. The mean value of the 8260 Method using all data was  $4.18 \pm 31.7$  mg/kg, whereas the mean value of the combined 8270 methods was  $0.326 \pm 1.20$  mg/kg (Table 1 and Figure 1). Using only the paired data for samples that had been analyzed with the 8270-SIM method, the mean for 8260 was  $4.09 \pm 35.1$  mg/kg and for 8270-SIM was  $0.363 \pm 1.14$  mg/kg (Figure 1). The data using non-SIM 8270 had a mean 8260 value of  $4.38 \pm 22.6$  mg/kg, and a mean 8270 value of  $0.245 \pm 1.33$  mg/kg (Figure 1).

**Table 1.** Minimum, Maximum, Mean, SD and Median concentrations of Naphthalene in soils using different sampling/analytical methods. All results in mg/kg.

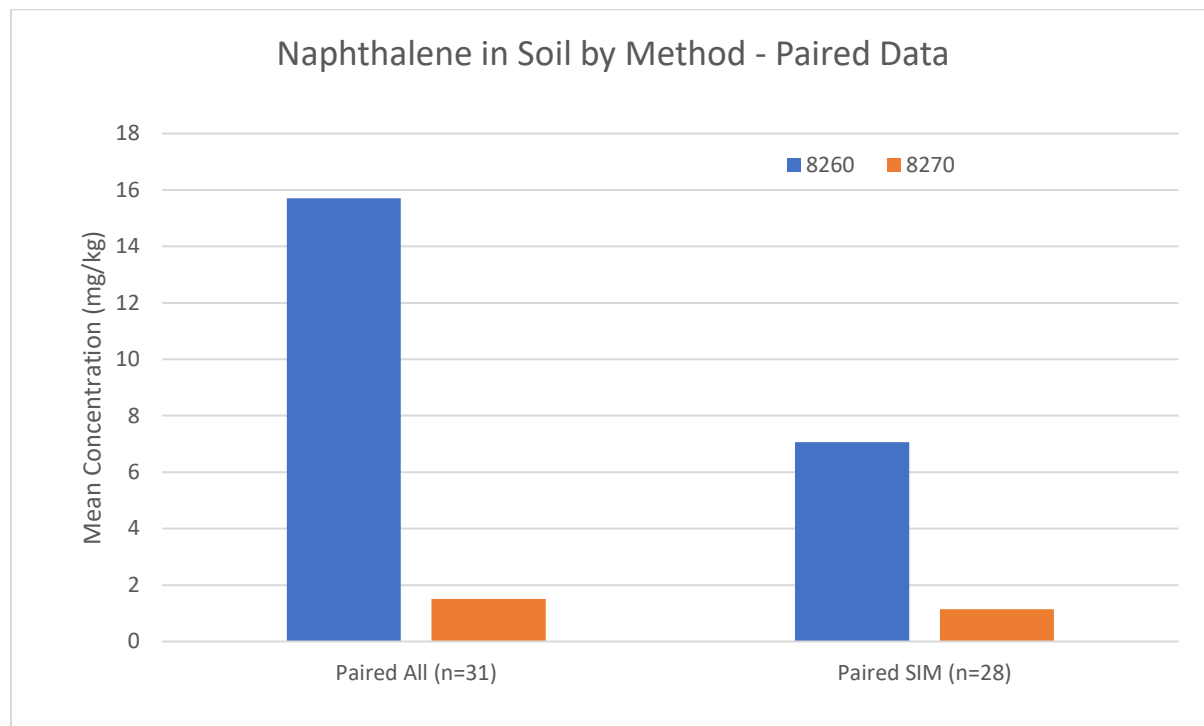
Method		Minimum	Maximum	Mean	SD	Median
All data (n=215)						
	8260	0	405	4.18	31.7	0
	8270	0	10.9	0.326	1.20	0.00976
SIM-only data (n=148)						
	8260	0	405	4.09	35.1	0
	8270	0	10.9	0.363	1.14	0.0815
Non-SIM data (n=67)						
	8260	0	151	4.38	22.6	0
	8270	0	9.3	0.245	1.33	0
Paired detections 8260 & 8270 (n=31)						
	8260	0.00257	151	15.7	39.6	0.79
	8270	0.00458	10.9	1.51	2.84	0.211
Paired detections 8260 & non-SIM (n=28)						
	8260	0.00257	138	7.06	26.0	0.713
	8270	0.0188	10.9	1.14	2.41	0.21



**Figure 1.** Mean Naphthalene soil concentrations for 8260 and 8270 methods using all paired data (left group), data with only 8270-SIM results (middle group) and data with only the non-SIM 8270 results (right group).

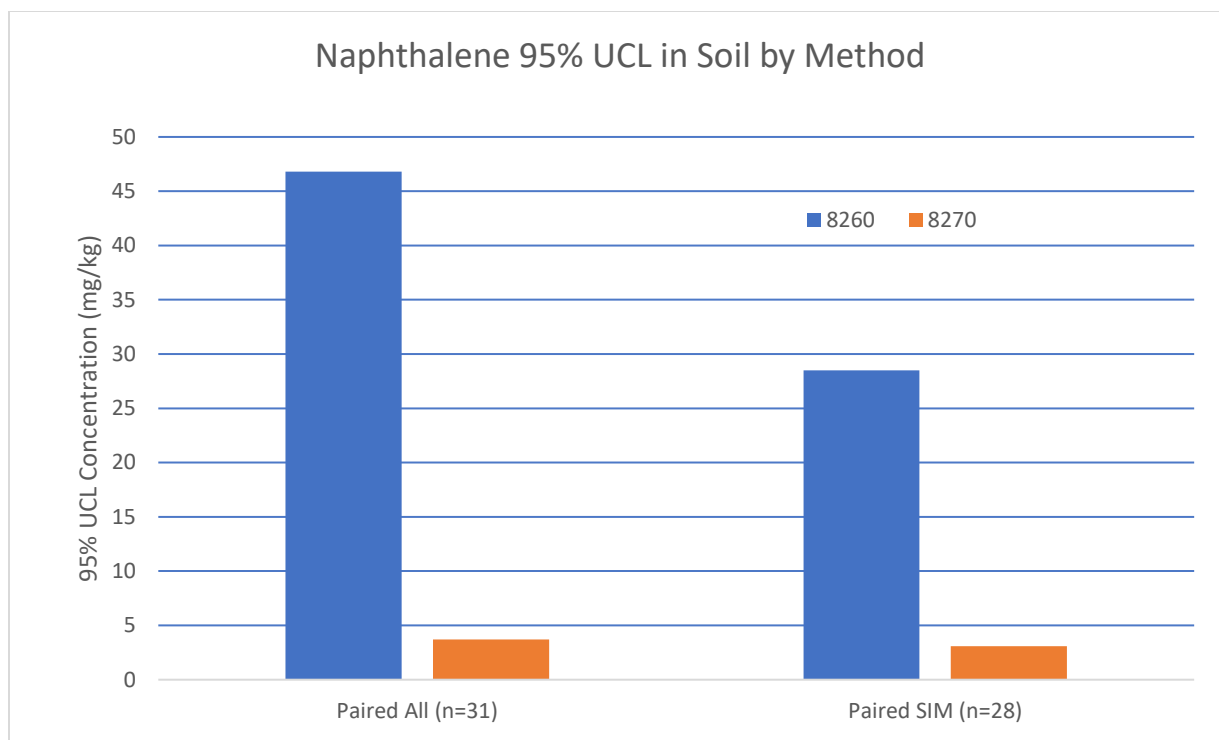
Comparing the datasets that had detections of Naphthalene using both the 8260 and 8270 methods (Figure 2) showed that the median Naphthalene concentration was significantly higher for the 8260 method (0.79 mg/kg) than for the 8270 method (0.211 mg/kg,  $U = 654$ ,  $p = 0.0149$ ). Additionally, comparing the 8260 data to 8270-SIM data for those that had detections using both methods (Figure 2)

also showed that the 8260 method (0.713 mg/kg) had a higher median than the 8270-SIM method (0.21 mg/kg,  $U = 528$ ,  $p = 0.0264$ ).



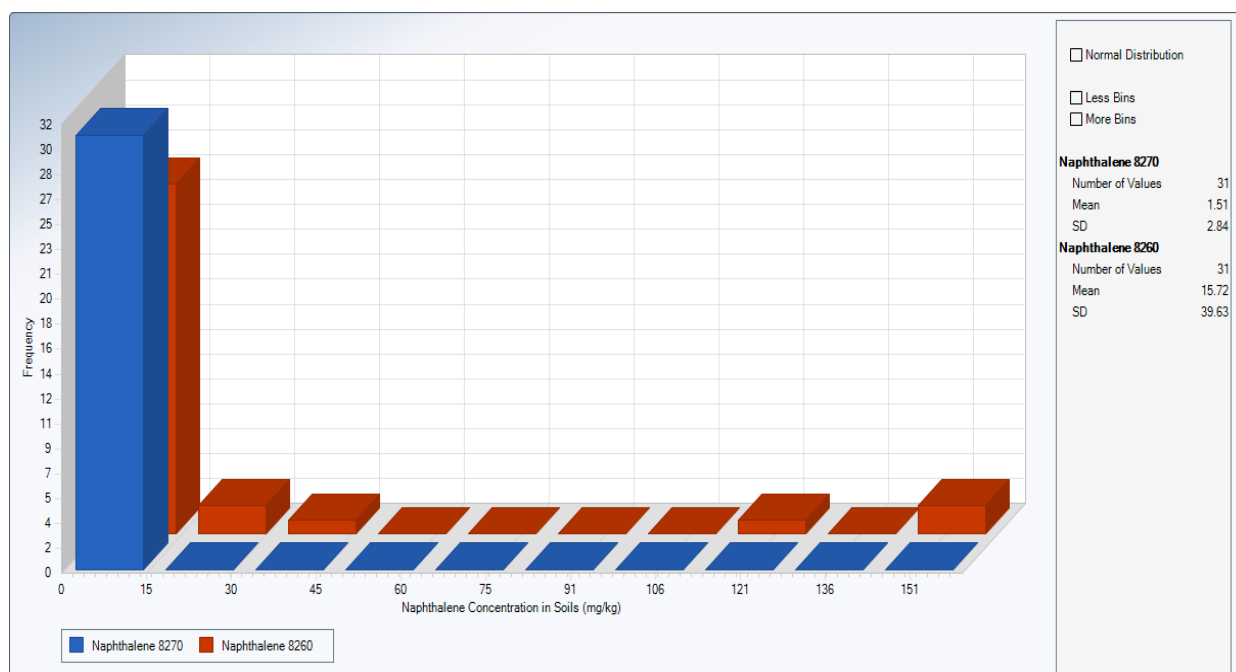
**Figure 2.** Mean Naphthalene soil concentrations for 8260 and 8270 methods using only paired data that had detections with both methods. The left group uses all 8270 method data and the right group uses only the 8270-SIM data. The 8260 results were significantly higher than the 8270 results using a 2-tailed Wilcoxon-Mann-Whitney test.

From a programmatic standpoint, the Exposure Point Concentrations (EPC) are typically based on the lowest of the maximum concentration for a specific medium or the 95% UCL following procedures outlined in ProUCL 5.1. The EPC then becomes the value used to make risk-based decisions about the need for remediation of the site. In this case, using all paired data resulted in a 95% UCL of 46.8 mg/kg via the 8260 method and 3.7 mg/kg via the 8270 method (Figure 3). Similarly, using just the data paired with 8270-SIM method, the 95% UCL was 28.5 mg/kg via the 8260 method and 3.1 mg/kg via the 8270-SIM method (Figure 3). These 95% UCL values would programmatically be compared to the WV Residential De Minimis Standard of 4.1 mg/kg for Naphthalene. The 8270 method results indicate that the site is acceptable for residential use, but the 8260 method results indicate that the site is unacceptable for residential use, indicating a programmatic conundrum.

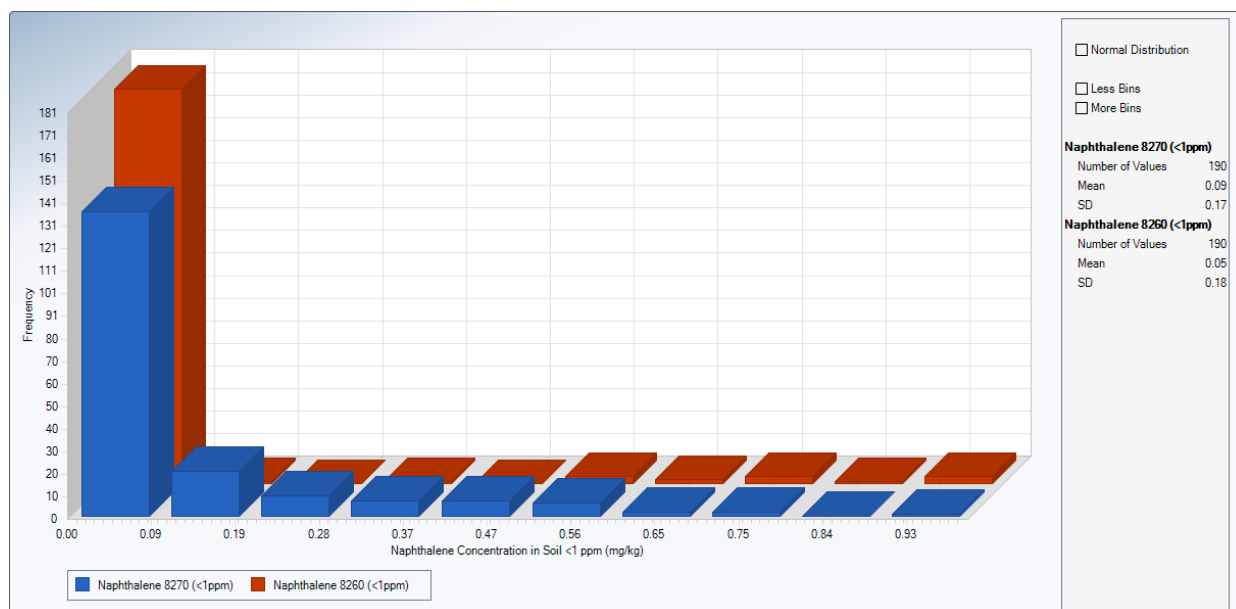


**Figure 3.** 95% UCL values for Naphthalene concentrations in soils analyzed using 8260 and 8270 methods. The left group uses all 8270 method data and the right group uses only the 8270-SIM data. The 8260 results exceeded the Residential De Minimis Standard of 4.1 mg/kg, but the 8270 methods were below the standard, limiting the confidence in programmatic decisions.

Using all data, the 8260 method had a 16.7% detection rate among the samples, while the 8270 method had a higher 52.6% detection rate. Similarly, assessing data that used the 8270-SIM method along with 8260 showed a 20.3% detection rate with the 8260 method and a 68.9% detection rate with the 8270-SIM method. The 8260 method also had a 9.0% detection rate compared to 16.4% for the paired non-SIM 8270 data. A histogram of the paired data with detections using both methods showed that the 8270 method had more detections of Naphthalene at the lower concentrations than the 8260 method (Figure 4). Conversely, the 8260 method had more detections of Naphthalene in the higher concentrations than the 8270 method. Further inspection of the data revealed that the 8260 method had very few detections with concentrations less than 1.0 mg/kg. In fact, most were non-detections, whereas the 8270 method had dozens of detections with concentrations less than 1.0 mg/kg (Figure 5).



**Figure 4.** Histograms of Naphthalene concentrations in soils (mg/kg) for EPA Methods 8260 and 8270 using data that had detections with both methods.



**Figure 5.** Histograms of Naphthalene concentrations in soils (mg/kg) for EPA Methods 8260 and 8270 using data with only results with concentration less than 1.0 mg/kg.

## Discussion

The data supported the hypothesis of higher concentrations of Naphthalene using the EPA 8260 Method, but that hypothesis does not necessarily mean that the differences are due to volatilization during soil homogenization. Further analysis showed that the 8260 method was still significantly higher

than just the 8270-SIM method, because only three samples that had both 8260 and 8270 results were analyzed using the non-SIM 8270 method.

The data similarly indicates that detections rates were generally higher using the 8270 methods, especially using SIM, and in the lower concentration range. These combined results indicate that the 8270-SIM method is better at detecting Naphthalene in soils with concentrations near the detection limit, which is not surprising given that the SIM method is designed specifically to enhance detection of PAHs in low concentrations (Mills 2020). However, the results also clearly show that the 8270-SIM method has lower results compared to the 8260 method, with a corresponding potential of false negatives at sites that analyze Naphthalene using only an 8270 method if they are biased low. Conversely, there may be false negatives using the 8260 method results if they are biased high. For example, the WVDEP Residential De Minimis Standard for Naphthalene is currently 4.1 mg/kg, indicating that sites with concentrations above this Standard usually require remediation before the site can be used for residential purposes. In this dataset, there were four pairs from three different sites that had concentrations below the Residential De Minimis Standard using the 8270-SIM method but concentrations above the Standard using the 8260 method, which would lead to conflicting interpretations and programmatic remedial decisions.

The source of the differences between the 8260 and 8270 method results is not known, and clearly an area in need of research. The higher concentrations using 8260 compared to 8270 may be due to the hypothesized volatilization of SVOCs during the homogenization process (EPA 2014). However, the differences may also be due to laboratory processes, such as method 3561 used to extract PAHs for 8270 analyses, and instrumentation that allow for a higher range of detections or promote/limit volatilization within the lab. Differences may even come from among personnel processing the samples within the lab. In four cases, the 8260 results were at least two orders of magnitude higher than the 8270-SIM results, but in one additional case the 8260 result was 405 mg/kg while the 8270-SIM result was non-detect. Such extreme cases may be from a general bias in the methods, but they may also be due to soil heterogeneity. The actual sample of soil going to the lab for the 8260 is obviously different than what is sent for the 8270 methods because they are collected in different containers, and there are also differences in subsample aliquots being analyzed. While the concentrations of Naphthalene in these nearby soil samples should be correlated, soils are notoriously heterogenous and the differences may simply be due to the random nature of contaminants in soil (Schumacher and Zimmerman 2004). However, such differences should be random, and cancel each other out in a larger dataset. In this case, a sample size of 31 may be large enough to cancel out random effects, but it cannot be completely ruled out since WVDEP does not know all of the specifics of how each sample was collected and prepare for analysis in the lab.

Given the common presence of Naphthalene at petroleum sites and the fact that it is often a driver of risk for those sites, the implications of a low bias are significant for the VRP and UECA/LUST programs. This issue may be compounded even further if the results are indicative of a general trend of a low bias among many/all SVOCs using the 8270 methods. Further research is needed to validate these results, determine the cause and extent of the bias and propose any necessary changes to the methods and/or standard operating procedures. WVDEP-OER recommends conducting a controlled study to determine the cause and magnitude of the differences by field and analytical methods. In the meantime, WVDEP-OER has requested that sites where Naphthalene is a Constituent of Potential Concern (COPC) sample for Naphthalene using both the 8260 and 8270 methods and the highest detected concentration will be used to represent a sample location when determining the Exposure Point Concentration. Note that in the six months since WVDEP required Naphthalene be analyzed using both 8260 and 8270 methods, several consultants have reported seeing the same differences in both soil and groundwater.

## References

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